

SUBSTITUTED METAL CARBONYLS

I. MOLYBDENUM CARBONYL COMPLEXES CONTAINING UNIDENTATE AND BRIDGING DIPHOSPHINES: ONE-POT SYNTHESSES

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Summary

Trimethylamine *N*-oxide (TMNO)-initiated decarbonylations of $\text{Mo}(\text{CO})_6$ followed by phosphine additions yield the complexes $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$, which consists of a unidentate diphosphine, and the dinuclear phosphine-bridged complexes $\text{Mo}_2(\text{CO})_{10}(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$ (where $n = 2, 3$) at ambient temperatures. The IR and NMR (^1H and ^{31}P) spectroscopic and structural properties of these complexes are presented and discussed. Some thermal analytical data are summarised.

Introduction

Mono- and di-substituted molybdenum carbonyl complexes are generally prepared by substitution reactions via a photolytic, thermolytic [1-4] or chemically-induced [5] route. While a large proportion of the current literature covers the above species, reports on the corresponding dinuclear complexes, which may be accessible by coupling reactions between the appropriate monomers, are relatively rare [6]. Using diphosphines as ligands and trimethylamine *N*-oxide (TMNO) as initiator, the present investigation aims to design a generally applicable synthetic pathway which can be carried out at room temperature for the above-mentioned systems and to study their relative chemical and thermal stabilities.

Results and discussion

Decarbonylation of $\text{Mo}(\text{CO})_6$ is induced by a stoichiometry quantity of TMNO in acetonitrile at room temperature or 0°C . Addition of dppm, dppe and dppp* to

* dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane.

TABLE 1
 ANALYTICAL AND SPECTROSCOPIC DATA

Complex (M.p. (°C))	Microanalyses (Found (calc) (%))		ν (cm ⁻¹)	δ (¹ H) (ppm)	δ (³¹ P) (ppm)
	C	H			
Mo(CO) ₅ (dppm) (1) (164)	58.14 (58.07)	3.64 (3.55)	2069m, 1996m, 1932vs(br) ^a	7.16–7.54(m,20H), 3.19(dd,2H); <i>J</i> (HP _a) 8.0Hz, <i>J</i> (HP _b) 2.7Hz.	28.34(d,1P), –24.97(d,1P); <i>J</i> (PP) 112Hz.
Mo ₂ (CO) ₁₀ (dppe) (2) (187, dec)	50.19 (49.90)	2.76 (2.73)	2072m, 1995m, 1928vs(br) ^a	7.25–7.39(m,20H), 2.20(br)(s,2H)	32.31(s,2P)
Mo ₂ (CO) ₁₀ (dppp) (3) (183, dec)	50.33 (50.20)	2.94 (2.92)	2070w, 1991w(sh), 1945vs(br) ^b	7.13–7.41(m,20H), 2.34(m,4H), ca. 1.42(br)(m,2H)	27.59(s,2P)

^a KBr disc. ^b CH₃CN.

the activated mixture, containing Mo(CO)₅(CH₃CN), gives rise to white crystalline products of Mo(CO)₅(dppm), **1**, Mo₂(CO)₁₀(dppe), **2**, and Mo₂(CO)₁₀(dppp), **3**, in yields of respectively 56, 56 and 62%. Detailed spectroscopic data of these complexes are summarised in Table 1.

Compound **1** represents the analogue of the known complexes Cr(CO)₅(dppm) [7] and W(CO)₅(dppm) [8]. Like all the other monosubstituted carbonyls, the compound possesses a C_{4v} symmetry [9] which is inferred by a strong and broad (E and A₁) and two weak-medium (A₁ and B₁) carbonyl absorption bands in the IR spectra. The presence of a dangling phosphine is confirmed by two phosphorus signals in the ³¹P NMR spectrum with a P–P coupling of 112 Hz. The uncoordinated phosphorus nucleus resonates at a frequency of –24.97 ppm, close to that of free dppm (δ –21.67 ppm). Compound **1** is readily formed in the reaction mixture even at 0°C. This contrasts sharply with the commonly adopted thermolytic route for other substituted carbonyls, which is carried out in refluxing 1,2-dimethoxyethane [4]. There is no infrared evidence for the formation of any bridging carbonyl intermediates. Interestingly, in contrast to **2** and **3**, the phosphine-bridged complex Mo₂(CO)₁₀(μ -dppm) apparently is not formed even at a reduced dppm concentration. It seems that close proximity of the two Mo(CO)₅ moieties is not favoured by a dppm bridge which must then bear a small bite angle. However, single phosphine-bridge complexes Mo₂(CO)₆(L)₂(μ -dppm) (where L = phen, bipy) [10] have been reported in the literature although their characterisations lacked firm spectroscopic support. In the presence of a stoichiometric amount of TMNO, **1** can be readily decarbonylated at room temperature to yield the known chelate Mo(CO)₄(dppm) [11,12].

Compound **3** is novel but compound **2** has been briefly reported [6,13]. Both complexes consist of a dinuclear skeleton supported by a diphosphine bridge. Similar to **1**, formation of **2** and **3** is facile. During their preparations, an increase in the concentration of free phosphines failed to generate the known mononuclear complexes Mo(CO)₅(dppe) [14,15] and Mo(CO)₅(dppp) [16] in detectable quantities. Shaw et al. [17] recently succeeded in isolating an interesting 10-membered ring complex Mo₂(CO)₈(μ -dppe)₂. This dinuclear complex, similar to **2** and **3**, was also reported to be very stable. There is no evidence for its formation under our experimental conditions, nor does it form from a mixture of **2** and free dppe at

room temperature. A fundamental difference in the stability of the dimers **2** and **3** from that of their respective monomeric species and the dppm analogue would be a subject of interest.

Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) studies of the three complexes [18] suggested a decomposition pathway which involves a stepwise cleavage of the Mo–C and Mo–P bonds. The TG thermogram of **1** shows a rapid weight loss between 180 to 200°C which corresponds to the elimination of one CO ligand (obs 4.8%; calc 4.6%). The steep weight loss which accompanied the increase in temperature up to 400°C is consistent with the rapid decomposition of the dppm ligand (obs 61.9%; calc 62%). Two of the remaining carbonyl ligands are expelled between 400 and 850°C (obs 10%; calc 9%). The weight remaining at 1000°C is consistent with the residue Mo(CO)₂. The DSC study revealed that the first endothermic peak at 164.95°C is very sharp and represents the melting of the complex. The second endothermic peak at 193.67°C confirms the expulsion of one CO ligand as indicated by TG. The low enthalpy value for this process (32.74 kJ mol⁻¹) suggests that the first CO ligand expelled, was very labile. The broad exothermic peak between 300 and 400°C can be attributed to the decomposition of the dppm ligand. The energy required for this step is 225.12 kJ mol⁻¹. A detailed interpretation of these data can be found in a separate report [18], which includes an in-depth comparison with its chromium and tungsten analogues. However, three key points can be summarised here:

- (i) The observation of such sequential degradations of the phosphine substituted metal carbonyls is unprecedented in the literature. The importance of thermal techniques such as TG and DSC in studying the structural and electronic nature of metal carbonyls should be realised.
- (ii) Facile cleavage of the first Mo–CO bond and its occurrence prior to that of the Mo–P bond is in full accord with the findings in some solution studies [2].
- (iii) The generation of highly unsaturated fragments such as Mo(CO)₄, Mo(CO)₃ and Mo(CO)₂ is intriguing and potentially useful. These species are not normally accessible through classical photolytic and thermolytic solution techniques as the fragments formed are too reactive. Contemporary methods such as laser pyrolysis [19,20,21] recently has been found to be effective in generating such reactive photofragments.

No quantitative analyses have been carried out on **2** or **3**. However, the TG thermograms of the two complexes display a similar stepwise decarbonylation and dephosphination. The occurrence of the former process proceeds more readily than the latter. While decarbonylation commences below 200°C for all the three complexes, however, dephosphination seems to occur more readily in **1** than in **2** and **3**.

Conclusion

TMNO is found to be effective in controlling the degree of substitution of Mo(CO)₆ by diphosphines. By varying the chain length of the latter, mononuclear or phosphine-bridged dimetal species may be isolated in reasonable yields at ambient or depressed temperature. The generalisation of the methodology for the synthesis of other Group VIB diphosphine substituted carbonyls are currently under investigation. Beside classical spectroscopic methods, thermal techniques, such as TG and DSC, are judged to be invaluable in providing crucial kinetic and thermo-

dynamic data on these systems. Such data could clearly contribute to a thorough understanding of the bonding and structural properties of metal carbonyls.

Experimental

(1) General procedures

All reactions were performed under pure dry dinitrogen using standard Schlenk techniques. Solvents were reagent grade and degassed before use. Proton NMR spectra were recorded on a JEOL FX 90Q at 89.55 MHz using $(\text{CH}_3)_4\text{Si}$ as internal standard. Phosphorus-31 NMR spectra were recorded on the same spectrometer at 36.23 MHz. Chemical shifts are reported in ppm to high frequency of external 85% phosphoric acid. The samples were run in deuterated chloroform. Infrared spectra were run on a Perkin-Elmer 1310 Infrared Spectrophotometer as solutions or on an FT-IR Perkin-Elmer 1710 IR spectrometer as KBr discs. Thermogravimetry was carried out under dinitrogen using a Shimadzu Thermal Analyzer DT-30 with a heating rate of 5–10°C/min. The differential scanning calorimetric study was performed on a DuPont 910 Differential Scanning Calorimeter. Detailed thermal data and experimental conditions can be found in ref. 18. Melting points were measured using a Büchi 512 melting point apparatus without calibration. Elemental analyses were performed by the Analytical Service of this department. All the instruments mentioned above are available from this department. Analytical and spectroscopic (NMR and IR) data are given in Table 1 together with the melting points. Phosphine ligands were purchased from Aldrich Chemical Co. and were checked for purity by ^{13}C and ^{31}P NMR before use. Molybdenum hexacarbonyl and trimethylamine *N*-oxide dihydrate were supplied from Aldrich Chemical Co. and Tokyo Kasei Kogyo Co. Ltd., respectively and used without further purification.

(2) Reactions

(a) $\text{Mo}(\text{CO})_5(\text{dppm})$. $\text{Mo}(\text{CO})_6$ (0.5072 g, 1.92 mmol) and TMNO (0.2103 g, 1.89 mmol) were stirred in acetonitrile (30 ml) at 28°C for 15 min, yielding a clear yellow solution. Upon addition of dppm (0.7299 g, 1.90 mmol) a light brown solution resulted. After 1 h of vigorous stirring, the milky suspension formed was filtered. The white solid obtained was washed with methanol and recrystallised from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. Yield: 0.68 g (56%).

(b) $\text{Mo}_2(\text{CO})_{10}(\text{dppe})$. TMNO (0.2143 g, 1.93 mmol) was added to a suspension of $\text{Mo}(\text{CO})_6$ (0.5071 g, 1.92 mmol) in acetonitrile (30 ml) at 0°C. With vigorous stirring a yellow colour steadily developed over 20 min. To this solution was added dppe (0.3820 g, 0.96 mmol), and the resulting light-brown solution was kept at –15°C for 15 h. The mixture was reduced in volume to ca. 10 ml and filtration yielded white microcrystals. Yield: 0.46 g (56%). The product can be recrystallised from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$.

(c) $\text{Mo}_2(\text{CO})_{10}(\text{dppp})$. A similar procedure was adopted as for $\text{Mo}_2(\text{CO})_{10}(\text{dppe})$. White microcrystals (yield 0.52 g (62%)) were obtained from $\text{Mo}(\text{CO})_6$ (0.5005 g, 1.89 mmol), TMNO (0.2168 g, 1.95 mmol) and dppp (0.3905 g, 0.95 mmol).

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